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Phosphorus distribution and availability within soil water-stable aggregates as affected by long-term fertilisation

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Abstract: A field experiment lasting 37 years was conducted to evaluate the applications of different rates of pig manure and mineral fertilisers alone or in combination impacts on total phosphorus (P_{total}) and Olsen phosphorus (P_{Olsen}) contents and phosphorus activity coefficient (PAC, percentage of P_{Olsen} to P_{total}) within soil water-stable aggregates (WSA) in a Mollisol of Northeast China. The contents of P_{total} and P_{Olsen} associated with different size classes of WSA significantly ($P < 0.05$) increased with an increasing rate of applied P. The application of manure alone or combined with mineral fertilisers significantly increased PAC value associated with different size classes of WSA. There were positive correlations between P_{total} and P_{Olsen} contents with soil organic carbon (SOC) content within soil WSA. As SOC content increased 1 g/kg, P_{total} and P_{Olsen} contents increased 0.06–0.10 g/kg and 7.69–22.2 mg/kg, respectively, and the increase was larger in smaller size classes of WSA. The results suggested that a high manure rate combined with mineral fertilisers is more beneficial for increasing soil phosphorus content and availability. SOC is a vital factor controlling phosphorus content and availability within soil WSA.

Keywords: maize monoculture; superphosphate; organic amendment; soil aggregate fractionation; soil organic matter

Phosphorus (P) is an essential nutrient for crop growth. For achieving optimum crop yield, mineral P fertilisers are widely applied to the soil. However, mineral P fertilisers are easily fixed after they are applied to the soil, and only 20% or less P is removed during the first year's crop growth, which leads to frequently excessive application of mineral P fertilisers (Alam et al. 2002) and subsequently may causes waterbody eutrophication (Bai et al. 2013). On the other hand, global phosphate rock resources used to produce mineral P fertilisers are finite and may be depleted by 2050 (Vance et al. 2003). Therefore, it is necessary to increase soil P availability for sustainable use and optimal management of P resources.

As an important soil quality indicator, soil aggregates are formed by the cementation of soil mineral particles and organic matter and regulate the distribution and availability of soil nutrients (Cui et al. 2019). The P distribution and availability within soil aggregates are also important for evaluating potential P loss through runoff (Mitran et al. 2018). In agroecosystems, fertilisation is the main factor affecting P distribution

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and availability in soil aggregates. Previous studies mainly focused on long-term fertilisation impacts on P forms and availability in bulk soil. There were relatively little and inconsistent findings of long-term fertilisation, particularly manure application rates, impacts on P distribution, and availability within soil water-stable aggregates (WSA) in agroecosystems.

In a previous study, Zhang et al. (2020) examined the impacts of long-term applications of different rates of pig manure alone or combined with mineral fertilisers on aggregate stability and associated soil organic carbon (SOC) content in a Mollisol. This study evaluates total phosphorus (P_{total}) and Olsen phosphorus (P_{Olsen}) contents and phosphorus activity coefficient (PAC) value responses to the fertilisation regimes in bulk soil and soil WSA in this long-term fertiliser experiment. Moreover, the relationships between P_{total} and P_{Olsen} contents and PAC value with SOC content were also examined. We hypothesised that (1) a high rate of pig manure combined with mineral fertilisers will be more beneficial to increase soil P contents and availability, and (2) P contents and availability increase with increasing SOC content due to the coupling relation between carbon and phosphorus.

MATERIAL AND METHODS

Experimental design and soil sampling. The long-term experiment with maize monoculture was started in 1980 at the National Monitoring Base of Soil Fertility and Fertiliser Efficiency on Mollisol (43°30'N, 124°48'E), Jilin province, China. The area has an annual average temperature of 5.5 °C and annual precipitation of 450–650 mm. The Mollisol was clay loam in texture, and the initial topsoil (0–20 cm) had a pH 7.6, SOC 16.3 g/kg, total nitrogen (N_{total}) 1.90 g/kg, P_{total} 0.61 g/kg, and P_{Olsen} 9.55 mg/kg.

In this study, six fertilisation treatments with three replicates per treatment were selected: (1) CK (unfertilised control); (2) NPK (150 kg N/ha/year as urea, 33 kg P/ha/year as superphosphate (16% of P), and 62 kg K/ha/year as potassium sulfate); (3) M1 (30 t/ha/year of pig manure); (4) M1 + NPK; (5) M2 (60 t/ha/year of pig manure), and (6) M2 + NPK. Each replicated plot (100 m^2 in size) was arranged in a randomised block design. All of the superphosphate and potassium sulfate and one-third of urea were applied as basal fertilisers, and the remaining urea was top-dressed in early to mid-June. The pig manure with an average composition of 46.9 g C/kg, 4.70 g N/kg, and 1.87 g P/kg was annually applied in late October after maize harvest.

In October 2017, topsoil samples (0–20 cm) were taken from five randomly chosen sites in each plot and mixed into a composite sample. The field-moist soil samples were sieved to 10 mm. One part of subsamples was utilised for aggregates separation, and the remaining subsamples were used for other soil properties analysis. The maize yield and some selected soil properties were listed in Table 1. Soil pH was measured with PHS-3C pH meter (INESA Scientific Instrument, Shanghai, China) using a 1:2.5 suspension in H_2O, SOC content was determined using sulfuric acid and potassium dichromate oxidation method, and soil total nitrogen content was measured by Kjeldahl method (Lao 1988).

Analytical methods. Soil WSA were separated using wet-sieving procedure into large macroaggregates (> 2 mm), small macroaggregates (2–0.25 mm), microaggregates (0.25–0.053 mm), and silt + clay

Table 1. Maize yield and selected soil properties in 2017

Treatment	Maize yield (kg/ha)	pH	SOC (g/kg)	N_{total} (g/kg)	SOC/N_{total}
CK	4 201 ± 405^{e}	7.67 ± 0.15^{a}	16.5 ± 0.19^{f}	1.48 ± 0.04^{e}	11.2 ± 0.39^{a}
NPK	10 276 ± 219^{d}	7.67 ± 0.04^{a}	18.6 ± 1.07^{e}	1.70 ± 0.01^{d}	10.9 ± 0.56^{a}
M1	10 761 ± 490^{c}	7.52 ± 0.06^{b}	26.3 ± 1.83^{c}	2.56 ± 0.05^{c}	10.3 ± 0.51^{ab}
M1NPK	12 119 ± 505^{a}	7.24 ± 0.01^{c}	23.3 ± 0.89^{d}	2.42 ± 0.09^{c}	9.65 ± 0.73^{b}
M2	11 170 ± 162^{bc}	7.31 ± 0.06^{c}	30.5 ± 0.46^{b}	2.93 ± 0.06^{b}	10.4 ± 0.08^{ab}
M2NPK	11 489 ± 539^{b}	7.07 ± 0.07^{d}	34.0 ± 0.94^{a}	3.26 ± 0.21^{a}	10.4 ± 0.49^{ab}

Data (means ± standard deviation, n = 3) followed by different small letters in the column indicate significant differences (P < 0.05). SOC – soil organic carbon; N_{total} – total nitrogen; SOC/N_{total} – soil organic carbon to total nitrogen ratio; CK – unfertilised control; NPK – 150 kg N/ha/year as urea, 33 kg P/ha/year as multiple superphosphate (16% of P), and 62 kg K/ha/year as potassium sulfate; M1 – 30 t/ha/year of pig manure; M2 – 60 t/ha/year of pig manure

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fractions (< 0.053 mm) (Cambardella and Elliott 1993). Soil P_{total} and P_{Olsen} were extracted by digesting with concentrated $HClO_4$-H_2SO_4 (Olsen and Sommers 1982) and by using 0.5 mol/L $NaHCO_3$ (Olsen et al. 1954), respectively, and P contents in the extracts were tested with ammonium molybdate-ascorbic acid method (Lu 2000).

Statistical analysis was conducted using SAS 8.0 software (SAS Institute Inc., Cary, USA). Two-way ANOVA was used to detect fertilisation, WSA size classes, and their interaction impacts on soil P_{total} and P_{Olsen} contents and PAC value. Differences among means were separated by *LSD* (least significant difference) test ($P < 0.05$). Pearson correlation and regression analyses were used to detect relationships between P_{total} and P_{Olsen} contents and PAC value with SOC content ($P < 0.05$ and $P < 0.01$).

RESULTS AND DISCUSSION

P_{total}, P_{Olsen}, and PAC value in bulk soil. Compared with CK treatment, mineral fertilisers alone had no significant effects on P_{total} and P_{Olsen} contents and PAC value (Figure 1). At the same site, Zhang et al. (2014) found that P_{total} and P_{Olsen} contents in the soil were not significantly different after mineral fertilisers application compared to the control without fertilisation, in agreement with our results. This could be due to the balance between P input by fertilisers and P output by crop uptake.

Compared with the non-manured (i.e., CK and NPK) treatments, the application of manure significantly increased P_{total} and P_{Olsen} contents and PAC value (Figure 1). On the one hand, pig manure itself contains approximately 3.9–48.7 g/kg of P_{total}, in which inorganic and organic P accounted for 51–92% and 8–37% of P_{total}, respectively (He et al. 2016). On the other hand, some labile and recalcitrant P forms existed in pig manure (He et al. 2007). Moreover, the pig manure application could reduce adsorption and promote the dissolution of P bound to soil minerals (Li et al. 2020). Thus, manure application was a favour to increase P content and availability in soil. Among the manured treatments, P_{total} and P_{Olsen} contents were significantly higher in treatments with than without mineral fertilisers and with high than with low manure rate, and the highest PAC value was also observed in the M2NPK treatments (Figure 1), suggesting that a high rate of manure combined with mineral fertilisers was more beneficial to increase soil P content and availability.

P_{total}, P_{Olsen}, and PAC value in soil WSA. In our present study, the recovery rates of P_{total} and P_{Olsen} after soil WSA fractionation ranged from 83.4% to 105.9% and from 90.5% to 111.7%, with averages of 91.3% and 100.9%, respectively. The indirect de-

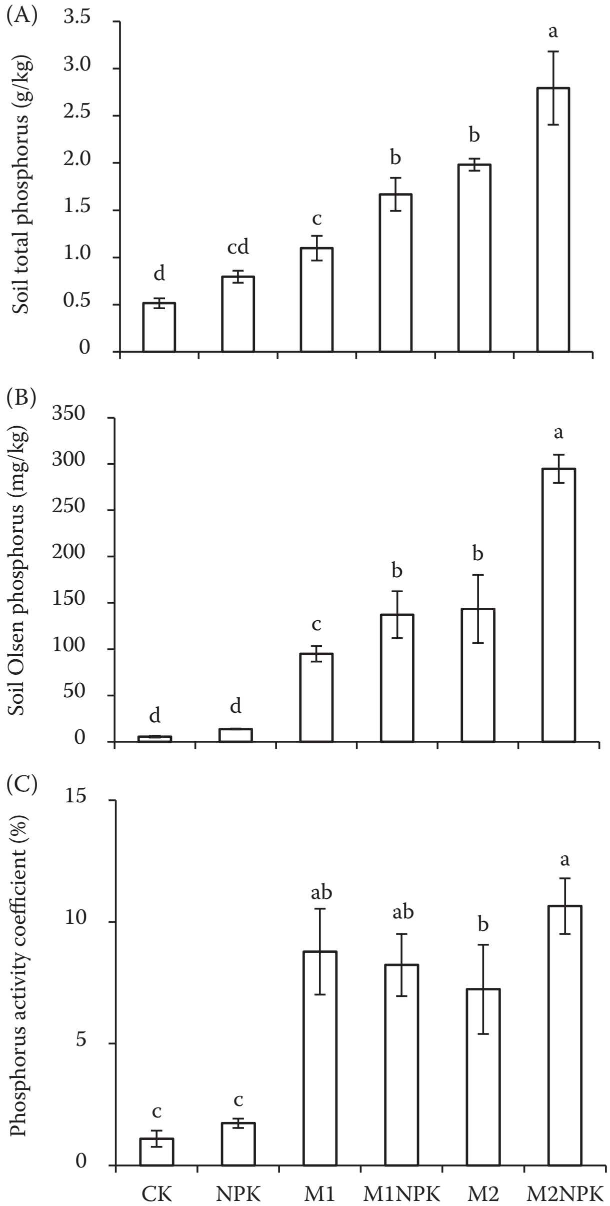

Figure 1. Effects of long-term fertilisation on (A) total phosphorus; (B) Olsen phosphorus contents, and (C) phosphorus activity coefficient in bulk soil. Vertical bars represent the standard deviation of the mean (n = 3). Different small letters indicate significant differences among fertilisation treatments (P < 0.05). CK – unfertilised control; NPK – 150 kg N/ha/year as urea, 33 kg P/ha/year as multiple superphosphate (16% of P), and 62 kg K/ha/year as potassium sulfate; M1 – 30 t/ha/year of pig manure; M2 – 60 t/ha/year of pig manure

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termination for the mass of silt + clay fractions by difference could lead to recovery rates greater than 100% in some cases.

The two-way ANOVA results showed that fertilisation, WSA size classes, and their interaction all have significant effects on P_{total} and P_{Olsen} contents (data not shown). Among different size classes, P_{total} and P_{Olsen} contents were not significantly different under CK and NPK treatments but were generally significantly lower in silt + clay fractions than in other size classes under M1, M1NPK, and M2 treatments; on the other hand, P_{total} and P_{Olsen} contents significantly increased in the order of silt + clay fractions < microaggregates < large macroaggregates < small macroaggregates and large macroaggregates < small macroaggregates < silt + clay fractions < microaggregates, respectively under NPKM2 (Figure 2A, B). Due to small WSA size classes are prone to run off and wind erosion (Cui et al. 2019), the lower P content in the silt + clay fractions under manure application could thus reduce release risk of P. In agreement with our hypothesis, P_{total} and P_{Olsen} contents within all WSA size classes increased in the order of CK < NPK < M1 < M1NPK < M2 < M2NPK. Our results were also consistent with previous findings that manure application increased P_{total} content within all size

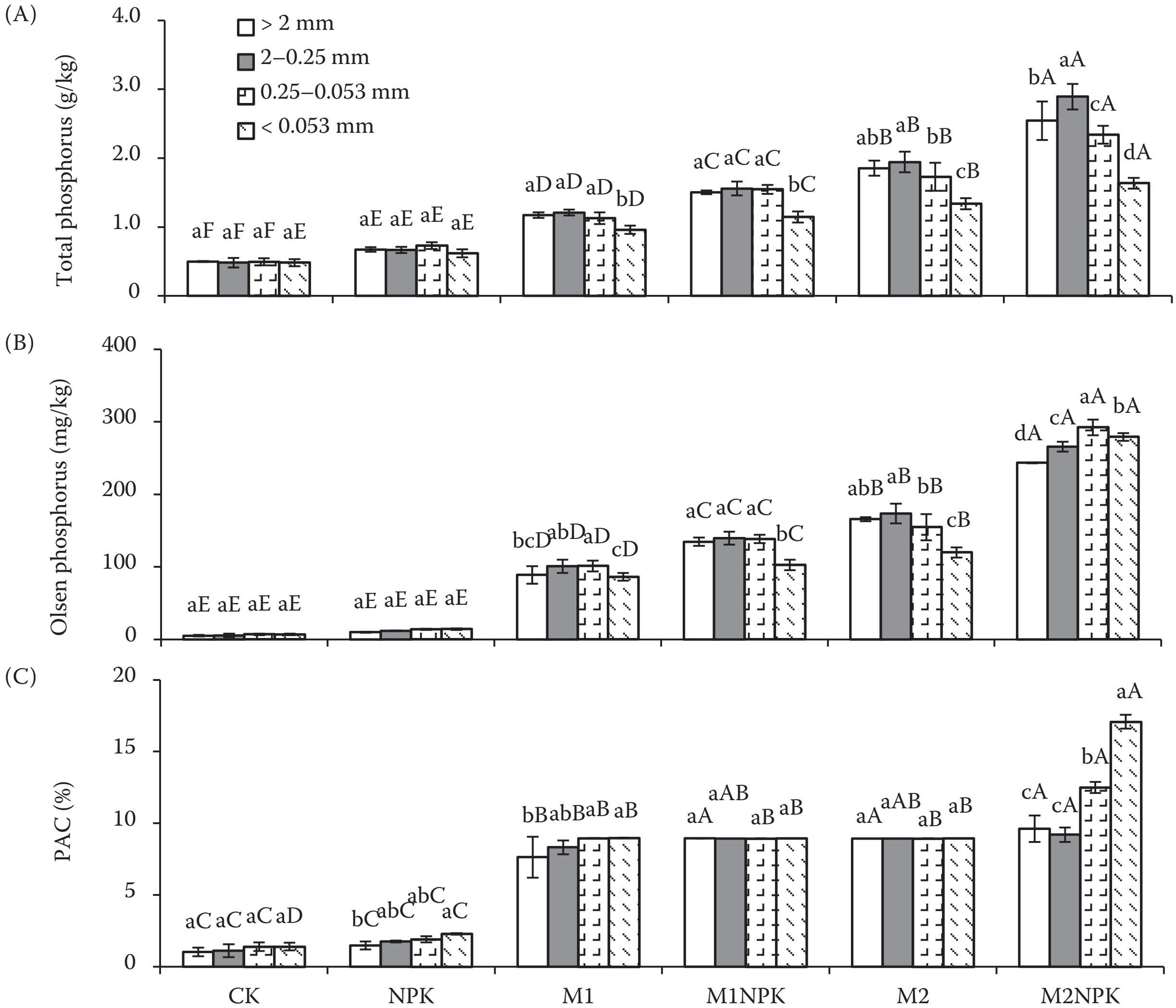

Figure 2. Effects of long-term fertilisation on (A) total phosphorus; (B) Olsen phosphorus contents and (C) phosphorus activity coefficient within soil aggregate size classes. Vertical bars represent the standard deviation of the mean (n = 3). The bars having different lowercase and uppercase letters denote significant differences among aggregate size classes and among fertilisation treatments, respectively (P < 0.05). CK – unfertilised control; NPK – 150 kg N/ha/year as urea, 33 kg P/ha/year as multiple superphosphate (16% of P), and 62 kg K/ha/year as potassium sulfate; M1 – 30 t/ha/year of pig manure; M2 – 60 t/ha/year of pig manure

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classes of WSA (Wang et al. 2011). No significant differences were observed between CK and NPK treatments for P_{total} associated with silt + clay fractions and for P_{Olsen} associated with all WSA size classes, which suggested that P_{total} balance occurred in the silt + clay fractions while P_{Olsen} balance appeared in all WSA size classes.

Fertilisation, WSA size classes, and their interaction also have significant effects on PAC value (data not shown). For different WSA size classes, PAC value was larger in silt + clay fractions than in macro- and microaggregates under all fertilisation treatments, and a significant difference was observed under M2NPK treatment (Figure 2C). The higher P availability in silt + clay fractions might be ascribed to the enrichment of P-cycling-related microorganisms within the size class (Wan et al. 2020), which also implied that larger WSA could protect P from mineralisation (Wright 2009). However, Wang et al. (2011) observed that PAC value was higher in large (> 2 mm) than in small (< 2 mm) WSA in paddy soil. The contradictory results might origin from the different P-cycling-related microbial activity under the upland and paddy field (Liu et al. 2018). Among fertilisation treatments, PAC value was not significantly different between CK and NPK treatments within macro- and microaggregates but was significantly greater under NPK than under CK treatment within silt + clay fractions. In contrast, manure application not only significantly increased PAC value in silt + clay fractions but also in macro- and microaggregates compared to the non-manured treatments. In agreement with our hypothesis, M2NPK treatment exhibited the highest PCA value, especially in silt + clay fractions. The improving microbial activity in silt + clay fractions enriching P-cycling-related bacteria (Wan et al. 2020) could contribute to the higher P availability within this size class under NPK and M2NPK treatment.

The contribution rates of P_{total} and P_{Olsen} associated with different WSA size classes to P_{total} and P_{Olsen} in bulk soil were distinct (Figure 3). In general, P_{total}

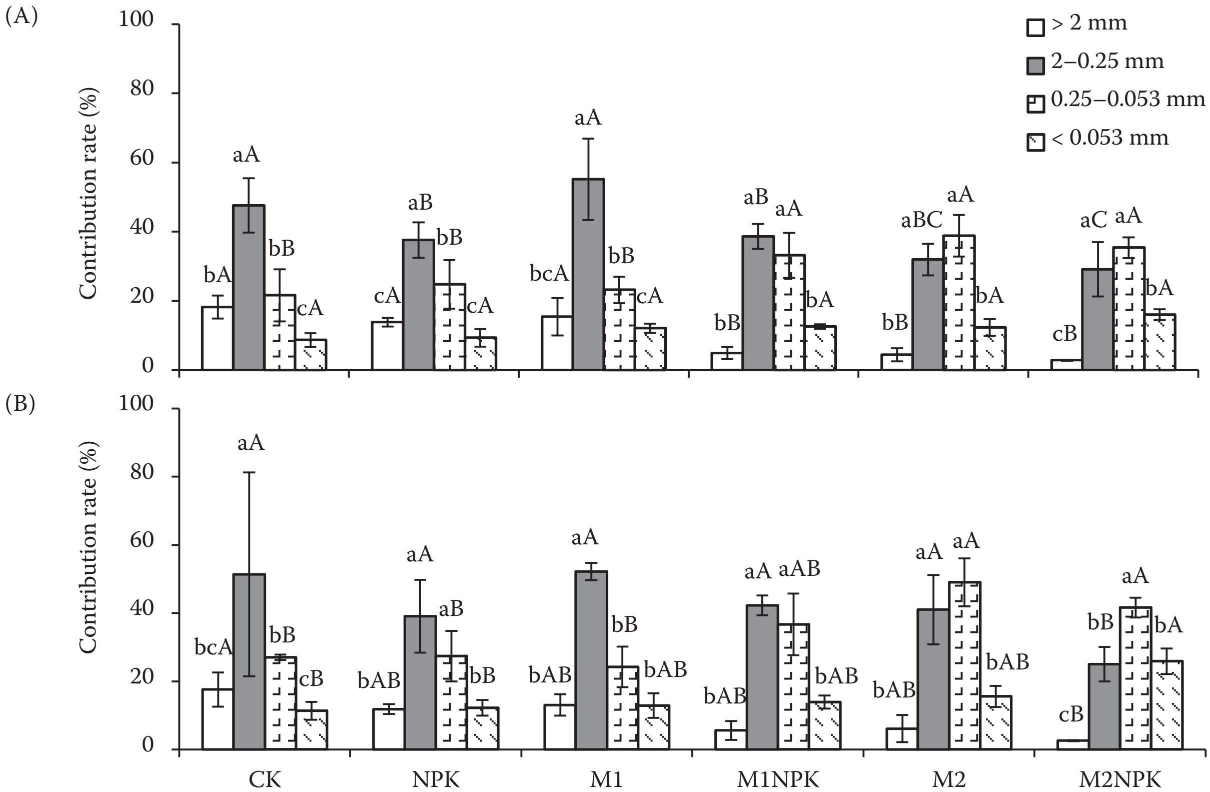

Figure 3. Effects of long-term fertilisation on contribution rates of (A) total phosphorus and (B) Olsen phosphorus within soil aggregate size classes to total phosphorus and Olsen phosphorus in bulk soil. Vertical bars represent the standard deviation of the mean (n = 3). The bars having different lowercase and uppercase letters denote significant differences among aggregate size classes and among fertilisation treatments, respectively (P < 0.05). CK – unfertilised control; NPK – 150 kg N/ha/year as urea, 33 kg P/ha/year as multiple superphosphate (16% of P), and 62 kg K/ha/year as potassium sulfate; M1 – 30 t/ha/year of pig manure; M2 – 60 t/ha/year of pig manure

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and P_{Olsen} associated with small macroaggregates and microaggregates contributed more than that associated with large macroaggregates and silt + clay fractions under all fertilisation treatments. Among fertilisation treatments, the contribution rates of P_{total} and P_{Olsen} associated with large- and small-macroaggregates were generally greater under CK, NPK, and M1 treatments than under M1NPK, M2, and M2NPK treatments; however, those of P_{total} and P_{Olsen} associated with microaggregates and silt + clay fractions were lower under CK, NPK, and M1 treatments than under M1NPK, M2, and M2NPK treatments. Our results suggested that higher P_{total} and P_{Olsen} contents under high manure rates were mainly from the contributions of microaggregates and silt + clay fractions.

Relationships between P_{total} and P_{Olsen} with SOC content in bulk soil and soil WSA. There were positive correlations between P_{total} content (r = 0.923, P < 0.01), P_{Olsen} content (r = 0.916, P < 0.05), and PAC value (r = 0.882, P < 0.05) with SOC content in bulk soil, which were consistent with our hypothesis that P contents and availability increase with increasing SOC content. Previous studies have found that SOC had a great effect on P mobilisation in soil (Wang et al. 2016, Romanyà et al. 2017). SOC decomposition could increase the release of P adsorbed on the soil surface (Méndez and Karlsson 2005), promote labile organic P mineralisation (Maharjan et al. 2018), and improve P mobilisation (Wang et al. 2011), which could explain the enhancing P availability with increasing SOC content.

P_{total} and P_{Olsen} contents were also positively correlated with SOC content within different WSA size classes (r = 0.914–0.977, P < 0.05 for P_{total} and r = 0.912–0.964, P < 0.05 for P_{Olsen}), which further confirmed our hypothesis. As SOC content increased 1 g/kg, the contents of P_{total} and P_{Olsen} within WSA increased 0.06–0.10 g/kg and 7.69–22.2 mg/kg, respectively (Figure 4A, B). With decreasing WSA size classes, the increases in P_{total} and P_{Olsen} contents became more obviously. On the other hand, SOC content was positively correlated with PCA value in microaggregates (r = 0.890, P < 0.05) and silt + clay fractions (r = 0.902, P < 0.05) but not in macroaggregates. With increasing SOC content, the larger slope for the silt + clay fractions (Figure 4C) further proved that silt + clay fractions with rich P-cycling-related microbes was more sensitive to the supply of carbon.

In conclusion, a high manure rate combined with mineral fertilisers is favour to increase P content and availability in bulk soil and soil WSA size classes, and the increasing P content and availability are mainly derived from the contributions of microaggregates and silt + clay fractions. The P content and avail-

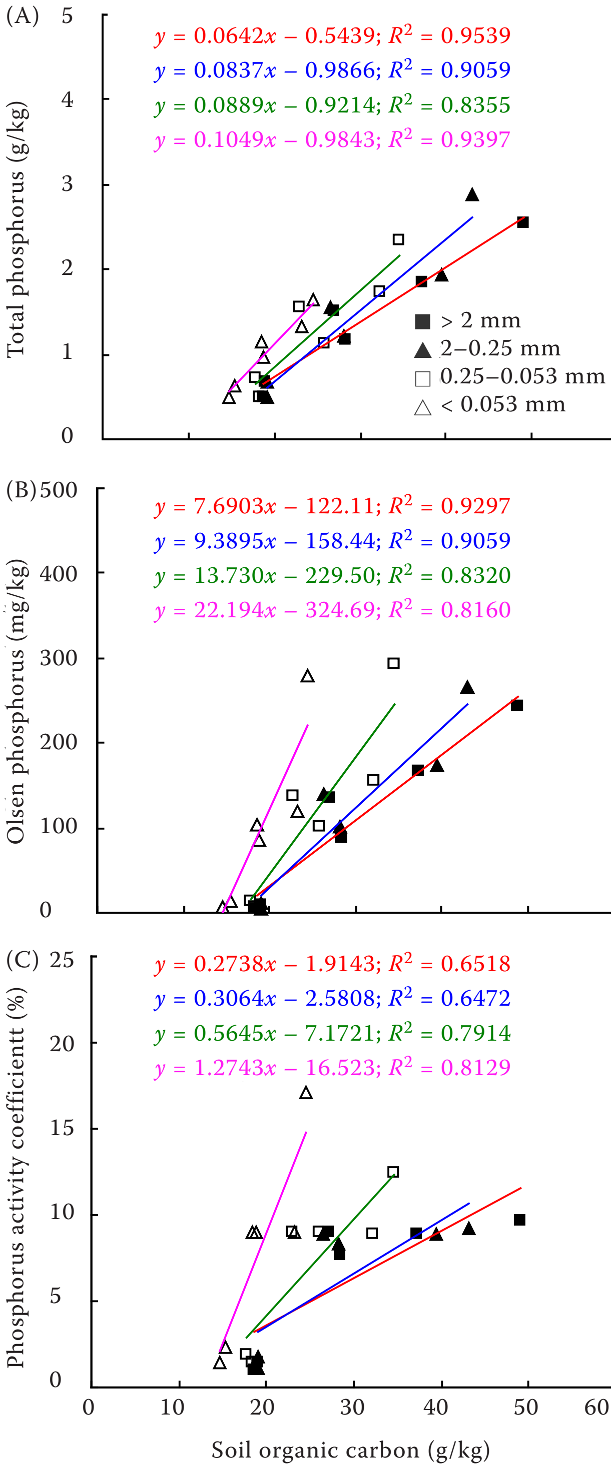

Figure 4. Relationships between (A) total phosphorus; (B) Olsen phosphorus, and (C) phosphorus activity coefficient with organic carbon contents within soil aggregate size classes

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ability increased with increasing SOC content, and the increase are larger in smaller size classes of WSA. However, further researches need to be performed under different soil-climatic conditions to confirm the present conclusions.

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